Analysis of lead and its alloys with the ARL iSpark OES spectrometer

The world leader in serving science
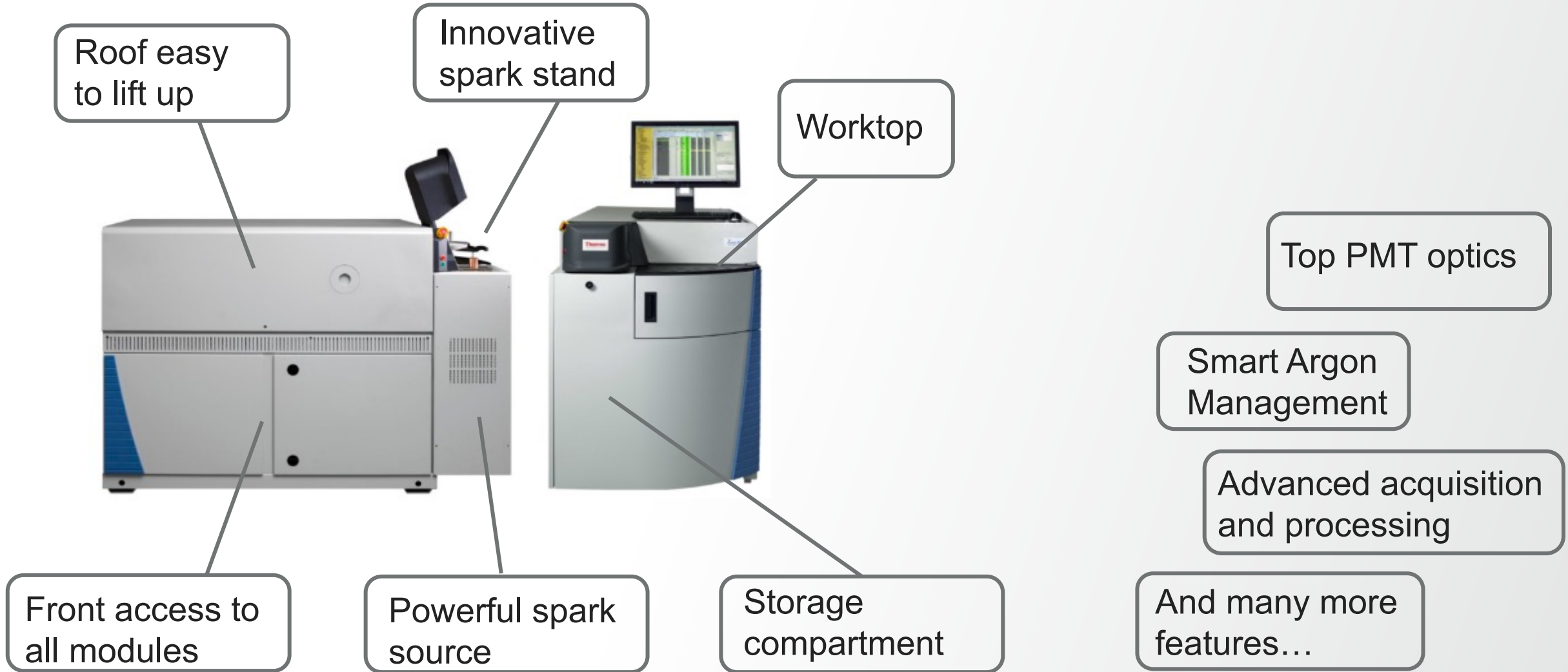
ARL iSpark 8860

The solution of choice
for elemental analysis of lead and its alloys

- High performance on trace and alloying elements
- True calibrations
- Advanced signal acquisition and processing modes
- Easy and fast stand maintenance
- Smart Argon Management tool
- Maintenance Management tool
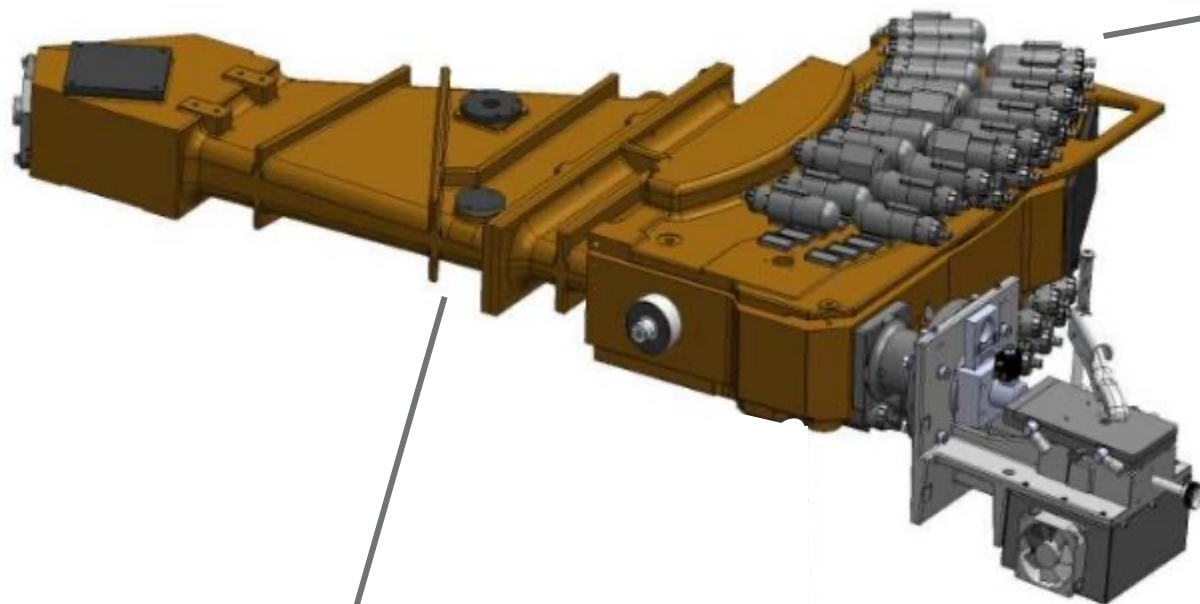- Synoptic tool for fast visual trouble-shooting
- Small effective footprint

ThermoFisher
SCIENTIFIC

ARL iSpark 8860

ARL iSpark 8860

The most famous spectrometer optics

PMT detectors
- Up to 80 PMTs
- Each with the most advanced technologies and processing algorithms
- Programmable high-voltage for each PMT

PMT optics
- 1m focal length Paschen-Runge for highest resolution
- Vacuum spectrometer for lowest sensitivity to external pressure
- Direct view for maximum light throughput
- Temperature-controlled cast iron spectrometer for highest stability

ARL iSpark 8860

Detectors

- Best photomultiplier tubes
  - $\varnothing$ 28 mm, side window circular cage type with 10 stages

PHOTOELECTRONS
GRID
INCIDENT LIGHT

0=PHOTOCATHODE
10=ANODE
1 to 9=DYNODES
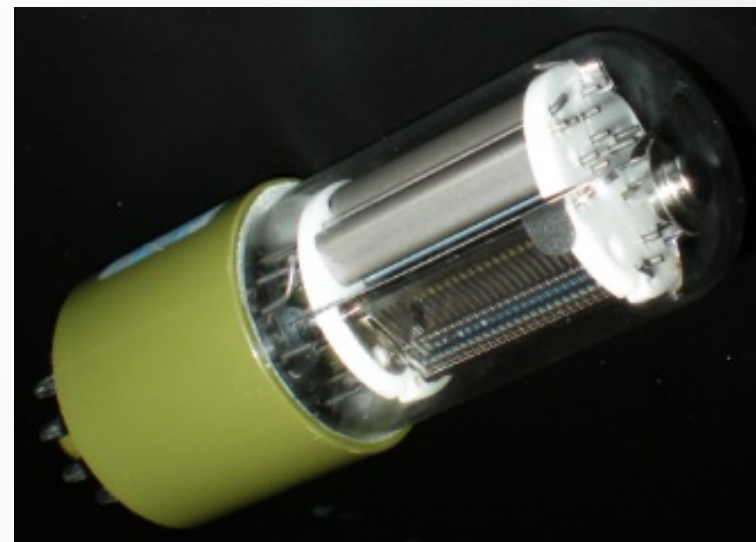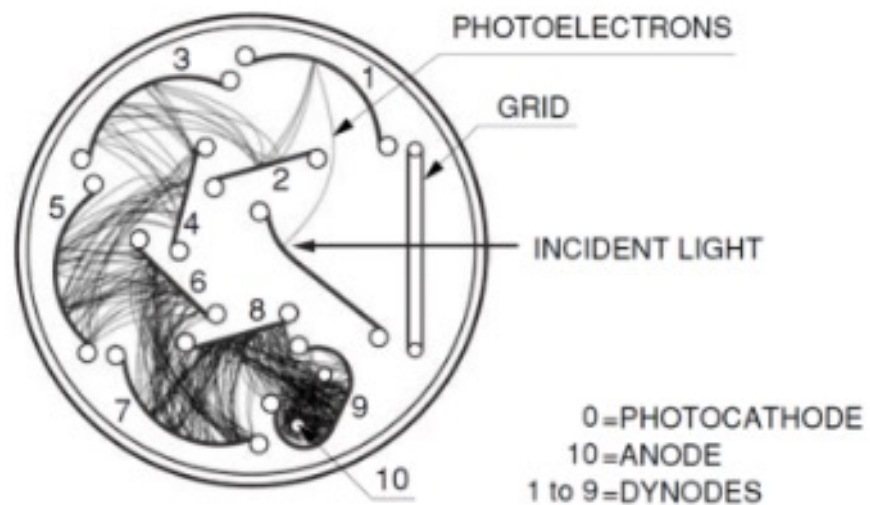
ARL iSpark 8860

Advanced acquisition and processing features

- With each PMT channel

  - Time Gated Acquisition (TGA), high precision TRS for improved performance and accuracy

  - Real-time PMT dark current and electronic offset subtraction

  - Single Spark Acquisition (SSA) allowing special data treatments

    – With DISIRE (DIffuse Spark Intensity REmoval) algorithm to improve repeatability and accuracy

    – With Spark-DAT algorithms for inclusion analysis
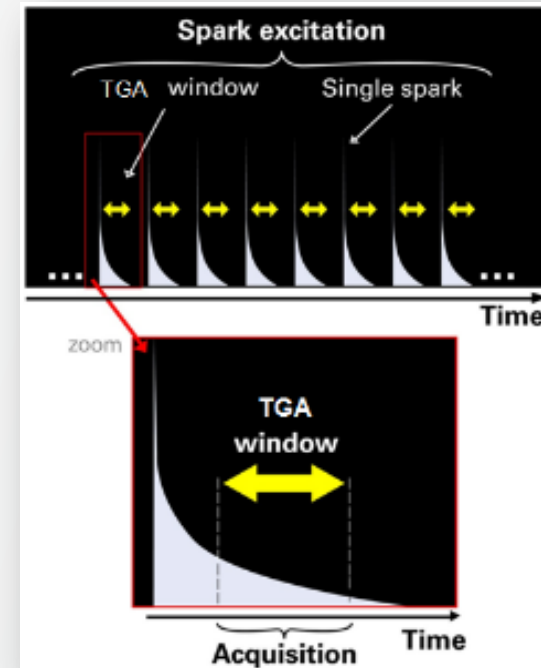
DISIRE
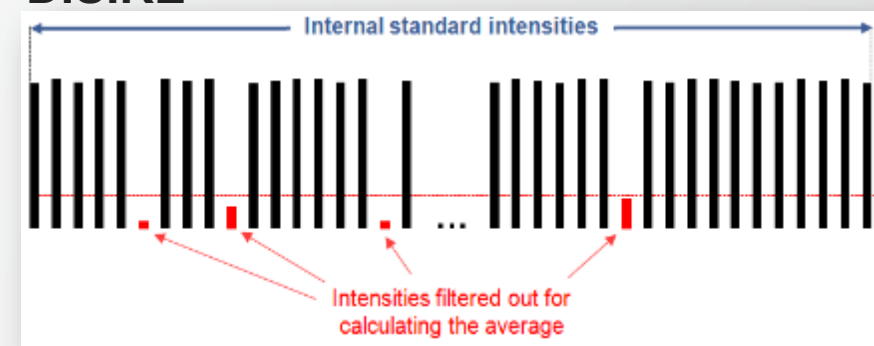
ARL iSpark 8860

Stand and spark source

- Innovative Spark stand design (patented)
  - Small volume spark chamber for low argon consumption
  - Fast cleaning and maintenance
    - No tool needed to dismantle and reassemble the stand

- IntelliSource (patented)
  - Powerful current controlled spark source (CCS)
    - High flexibility on spark shape
    - Better overall performance, less interferences, better accuracy

ARL iSpark 8860

High degree of functionality

- Worktop for samples and accessories
  accessories

- Storage compartment for rapid access to
  setting-up samples, accessories, log book…

- Front access to all parts of the instrument
  - Facilitates maintenance and service
  - Very little clearance needed behind
  - Instrument can be installed against a wall

8

ARL iSpark 8860

High degree of functionality

- Roof
  - Easy to lift up
  - No clearance needed behind

- Small effective footprint
  - ARL iSpark can be installed against a wall
  - And also in a corner

10 cm
4 inches

Analysis of lead and its alloys

Details and practical aspects

- Sample preparation: milling or turning
  - Grinding not recommended due to the risk of contamination

- Analytical material
  - Table hole diameter   15mm
  - Electrode diameter   4mm
  - Electrode cleaning with Mo brush

- Time of analysis (from start to result display)
  - Average time for one run   13.5s
  - Typical time for 3 runs* analysis including electrode cleaning 60-70s

* Minimum number of runs recommended in DIN V ENV 12908 (1998-01)

Analysis of lead and its alloys

Details and practical aspects

- Calibrations available for
  - Lead: pure and low alloyed lead
  - Lead alloys: Pb/Sn, PB/Sn/Sb, Pb/Sb battery and Pb/Ca battery
  - Global lead and lead alloys

- Elements
  - In standard: Ag, Al, As, Au, Bi, Ca, Cd, Cu, Fe, In, Ni, P, S, Sb, Se, Sn, Te, Tl, Zn
    - Calibrated mainly with CRMs
  - Also possible, e.g., Ba, Co, Cr, Ge, Hg, Ir, Mg, Na, Pd, Pt, Rh, Ru, Si
    - Calibrated with RMs

Analysis of lead and its alloys – Detection limits

Detection limits

DL [ppm]	Ag	Al	As	Au	Bi	Ca	Cd	Co	Cr	Cu	Fe	Ge	In
Typical	0.004	0.01	0.3	0.2	0.01	0.02	0.006	0.05	0.08	0.006	0.2	0.025	0.03
Guaranteed	0.008	0.025	0.5	0.3	0.03	0.05	0.01	0.1	0.2	0.015	0.4	0.05	0.05

DL [ppm]	Mg	Ni	P	Pd	Pt	S	Sb	Se	Sn	Te	Tl	Zn
Typical	0.002	0.01	2	0.01	0.2	0.5	0.2	0.7	0.2	0.35	0.02	0.1
Guaranteed	0.005	0.02	3		0.3	1	0.5	1	0.4	0.5	0.03	0.2

Values based on 10 repeated measurements, typically

- Typical DL is average DL of instruments produced, while guaranteed DL is DL guaranteed for 95% of the instruments produced

- Limit of quantification defines the lowest value of the calibration range (when calibration samples are available)

LOQ (3·DL) [ppm]	Ag	Al	As	Au	Bi	Ca	Cd	Co	Cr	Cu	Fe	Ge	In
Typical	0.012	0.03	0.9	0.6	0.03	0.06	0.018	0.15	0.24	0.018	0.6	0.075	0.09
Guaranteed	0.024	0.075	1.5	0.9	0.09	0.15	0.03	0.3	0.6	0.045	1.2	0.15	0.15

LOQ (3·DL) [ppm]	Mg	Ni	P	Pd	Pt	S	Sb	Se	Sn	Te	Tl	Zn
Typical	0.006	0.03	6	0.03	0.6	1.5	0.6	2.1	0.6	1.05	0.06	0.3
Guaranteed	0.015	0.06	9	0	0.9	3	1.5	3	1.2	1.5	0.09	0.6

The DL's of the ARL iSpark make it suitable for the quantitative determination of most trace elements requested according to current standards for lead and lead alloys

Analysis of lead and its alloys – Precision examples

Pure lead

NIST C2416 (CRM) (no run deleted)

NIST C2416	Pb	Sn	Sb	Bi	Cu	Cd	As	Zn	Ni	Ag	Ca	Fe	In	Se
Run 1	98.873	0.0983	0.799	0.102	0.0644	0.00031	0.0556	0.00002	0.00055	0.00407	0.00007	0.00005	0.00008	0.00008
Run 2	98.878	0.0983	0.796	0.100	0.0645	0.00032	0.0553	0.00002	0.00055	0.00394	0.00010	0.00005	0.00008	0.00014
Run 3	98.877	0.0989	0.796	0.099	0.0651	0.00033	0.0551	0.00002	0.00057	0.00391	0.00012	0.00005	0.00008	0.00017
Run 4	98.870	0.0973	0.805	0.100	0.0642	0.00031	0.0553	0.00002	0.00055	0.00400	0.00004	0.00005	0.00008	0.00008
Run 5	98.880	0.0974	0.795	0.100	0.0636	0.00031	0.0553	0.00002	0.00056	0.00401	0.00013	0.00006	0.00008	0.00012
Run 6	98.858	0.0995	0.810	0.102	0.0668	0.00033	0.0562	0.00002	0.00057	0.00410	0.00009	0.00006	0.00008	0.00013
Run 7	98.864	0.0974	0.812	0.099	0.0633	0.00032	0.0559	0.00002	0.00055	0.00403	0.00014	0.00005	0.00007	0.00024
Run 8	98.872	0.0979	0.801	0.100	0.0651	0.00032	0.0556	0.00002	0.00055	0.00403	0.00011	0.00005	0.00008	0.00016
Average	98.872	0.0981	0.802	0.100	0.0646	0.00032	0.0555	0.00002	0.00056	0.00401	0.00010	0.00005	0.00008	0.00014
SD	0.008	0.0008	0.007	0.0009	0.0011	0.00001	0.0004	0.000001	0.00001	0.00006	0.00003	0.000004	0.000002	0.00005
SD%	0.01	0.82	0.81	0.91	1.69	2.18	0.68	3.24	1.33	1.54	32.61	6.88	2.06	35.90

NIST C2416		Al	Te	Tl	S	Mg	Co	Au	Pt	Na	Cr	Ge	Hg	Pd
Run 1		0.00001	0.00061	0.00009	0.00155	0.00001	0.00002	0.00001	-0.00001	0.00007	0.00001	0.00013	0.00024	0.00007
Run 2		0.00001	0.00062	0.00009	0.00159	0.00001	0.00001	0.00001	0.00000	0.00008	0.00001	0.00013	0.00029	0.00008
Run 3		0.00001	0.00061	0.00009	0.00163	0.00001	0.00001	0.00003	0.00000	0.00008	0.00001	0.00013	0.00038	0.00008
Run 4		0.00001	0.00060	0.00009	0.00149	0.00001	0.00001	0.00002	0.00001	0.00007	0.00001	0.00013	0.00028	0.00007
Run 5		0.00001	0.00060	0.00009	0.00155	0.00001	0.00001	0.00001	-0.00001	0.00007	0.00001	0.00013	0.00032	0.00007
Run 6		0.00001	0.00062	0.00009	0.00155	0.00001	0.00001	0.00001	0.00000	0.00007	0.00001	0.00013	0.00033	0.00008
Run 7		0.00001	0.00062	0.00008	0.00164	0.00001	0.00001	0.00002	-0.00002	0.00007	0.00001	0.00013	0.00043	0.00007
Run 8		0.00001	0.00063	0.00009	0.00156	0.00001	0.00001	0.00002	-0.00002	0.00007	0.00001	0.00013	0.00034	0.00008
Average		0.00001	0.00061	0.00009	0.00157	0.00001	0.00001	0.00002	-0.00001	0.00007	0.00001	0.00013	0.00033	0.00007
SD		0.000001	0.00001	0.000001	0.00005	0.000000	0.00001	0.00001	0.00001	0.000002	0.00000	0.000001	0.00006	0.000001
SD%		13.87	1.78	0.80	3.14	2.43	49.96	27.85	115.02	3.17	3.71	0.88	17.94	1.61

BCR 286 (CRM) (7 runs, no run deleted)

BCR 286	Pb	Sn	Sb	Bi	Cu	Cd	As	Zn	Ni	Ag	Ca	Fe	In	Se
Average	99.996	0.00007	0.00003	0.00221	0.00014	0.00001	0.00019	0.00003	0.00002	0.000003	0.00001	0.00008	0.00008	0.00005
SD	0.0002	0.00002	0.00001	0.00003	0.000008	0.000004	0.00001	0.000001	0.000001	0.000002	0.000002	0.000004	0.000002	0.00004
SD%	0.00	32.69	27.98	1.13	5.27	29.43	7.69	3.55	2.88	38.71	27.12	5.94	2.13	64.98

BCR 286		Al	Te	Tl	S	Mg	Co	Au	Pt	Na	Cr	Ge	Hg	Pd
Average		0.00001	0.00005	0.00027	0.00009	0.00001	0.00002	0.00003	0.00002	0.00010	0.00003	0.00012	0.00039	0.00004
SD		0.000000	0.000005	0.000002	0.00002	0.000000	0.000004	0.000003	0.00001	0.000004	0.00004	0.000001	0.00008	0.000000
SD%		4.21	8.66	0.78	24.49	0.65	17.40	9.18	63.22	3.83	133.96	0.57	21.49	0.47

- Precision excellent on all elements at concentration > LOQ, except Ca (inhomogeneous)

Analysis of lead and its alloys – Precision examples

PbSb

• Precision is excellent, despite most elements at very low concentration

BAM E103 (CRM) (no run deleted)

BAM EB103	Pb	Sn	Sb	Bi	Cu	As	Zn	Ni	Ag	Ca	Fe	In
Run 1	97.943	0.181	1.735	0.0161	0.00086	0.097	0.00007	0.00033	0.00706	0.00001	0.00009	0.00011
Run 2	97.915	0.182	1.758	0.0162	0.00089	0.100	0.00007	0.00034	0.00725	0.00001	0.00010	0.00010
Run 3	97.945	0.182	1.732	0.0160	0.00086	0.097	0.00007	0.00033	0.00702	0.00001	0.00008	0.00010
Run 4	97.931	0.181	1.744	0.0160	0.00088	0.099	0.00007	0.00033	0.00717	0.00001	0.00009	0.00010
Run 5	97.947	0.180	1.731	0.0159	0.00085	0.098	0.00007	0.00033	0.00694	0.00001	0.00008	0.00010
Run 6	97.936	0.179	1.739	0.0160	0.00087	0.101	0.00007	0.00034	0.00707	0.00001	0.00008	0.00010
Run 7	97.951	0.181	1.726	0.0160	0.00085	0.097	0.00007	0.00033	0.00694	0.00001	0.00009	0.00010
Run 8	97.934	0.183	1.742	0.0162	0.00086	0.097	0.00007	0.00033	0.00711	0.00001	0.00009	0.00010
Run 9	97.924	0.180	1.749	0.0160	0.00088	0.102	0.00007	0.00034	0.00714	0.00001	0.00008	0.00010
Average	97.936	0.181	1.740	0.0161	0.00087	0.099	0.00007	0.00033	0.00708	0.00001	0.00009	0.00010
SD	0.012	0.0014	0.010	0.00010	0.000015	0.0019	0.000002	0.000006	0.000102	0.000001	0.00001	0.00000
SD%	0.01	0.76	0.57	0.63	1.7	1.93	2.87	1.89	1.44	6.26	8.48	2.38

BAM EB103		Se	Al	Te	Tl	S	Co	Au	Pt	Na	Cr	Ge
Run 1		0.0168	0.00001	0.00018	0.00150	0.00050	0.00003	0.00012	0.00012	0.0001	0.00013	0.00002
Run 2		0.0169	0.00001	0.00018	0.00152	0.00047	0.00002	0.00011	0.00012	0.0001	0.00013	0.00002
Run 3		0.0171	0.00001	0.00017	0.00152	0.00049	0.00003	0.00012	0.00012	0.0001	0.00011	0.00002
Run 4		0.0174	0.00001	0.00018	0.00153	0.00051	0.00003	0.00012	0.00012	0.0001	0.00012	0.00002
Run 5		0.0174	0.00001	0.00018	0.00150	0.00052	0.00003	0.00012	0.00011	0.0001	0.00011	0.00002
Run 6		0.0174	0.00001	0.00018	0.00150	0.00054	0.00003	0.00013	0.00012	0.0001	0.00014	0.00002
Run 7		0.0174	0.00001	0.00019	0.00152	0.00049	0.00004	0.00013	0.00011	0.0001	0.00013	0.00002
Run 8		0.0170	0.00001	0.00017	0.00154	0.00044	0.00003	0.00010	0.00013	0.0001	0.00009	0.00002
Run 9		0.0177	0.00001	0.0002	0.00150	0.00063	0.00003	0.00012	0.00009	0.0001	0.0001	0.00002
Average		0.0172	0.00001	0.00018	0.00152	0.00051	0.00003	0.00012	0.00012	0.0001	0.00012	0.00002
SD		0.0003	0.00000	0.00001	0.00001	0.00005	0.000004	0.00001	0.000012	0.000001	0.000017	0.000001
SD%		1.68	1.89	5.38	0.95	10.52	13.85	8.16	10.51	0.72	14.34	6.65

MBH 81X PA7.0 C (binary standard) – 8 runs (no run deleted)

BCR 286	Pb	Sn	Sb	Bi	Cu	Cd	As	Zn	Ni	Ag	Ca	Fe	In	Se
Average	99.996	0.00007	0.00003	0.00221	0.00014	0.00001	0.00019	0.00003	0.00002	0.000003	0.00001	0.00008	0.00008	0.00005
SD	0.0002	0.00002	0.00001	0.00003	0.000008	0.000004	0.00001	0.000001	0.000001	0.000002	0.000002	0.000004	0.000002	0.00004
SD%	0.00	32.69	27.98	1.13	5.27	29.43	7.69	3.55	2.88	38.71	27.12	5.94	2.13	64.98

BCR 286		Al	Te	Tl	S	Mg	Co	Au	Pt	Na	Cr	Ge	Hg	Pd
Average		0.00001	0.00005	0.00027	0.00009	0.00001	0.00002	0.00003	0.00002	0.00010	0.00003	0.00012	0.00039	0.00004
SD		0.000000	0.000005	0.000002	0.00002	0.000000	0.000004	0.000003	0.00001	0.000004	0.00004	0.000001	0.00008	0.000000
SD%		4.21	8.66	0.78	24.49	0.65	17.40	9.18	63.22	3.83	133.96	0.57	21.49	0.47

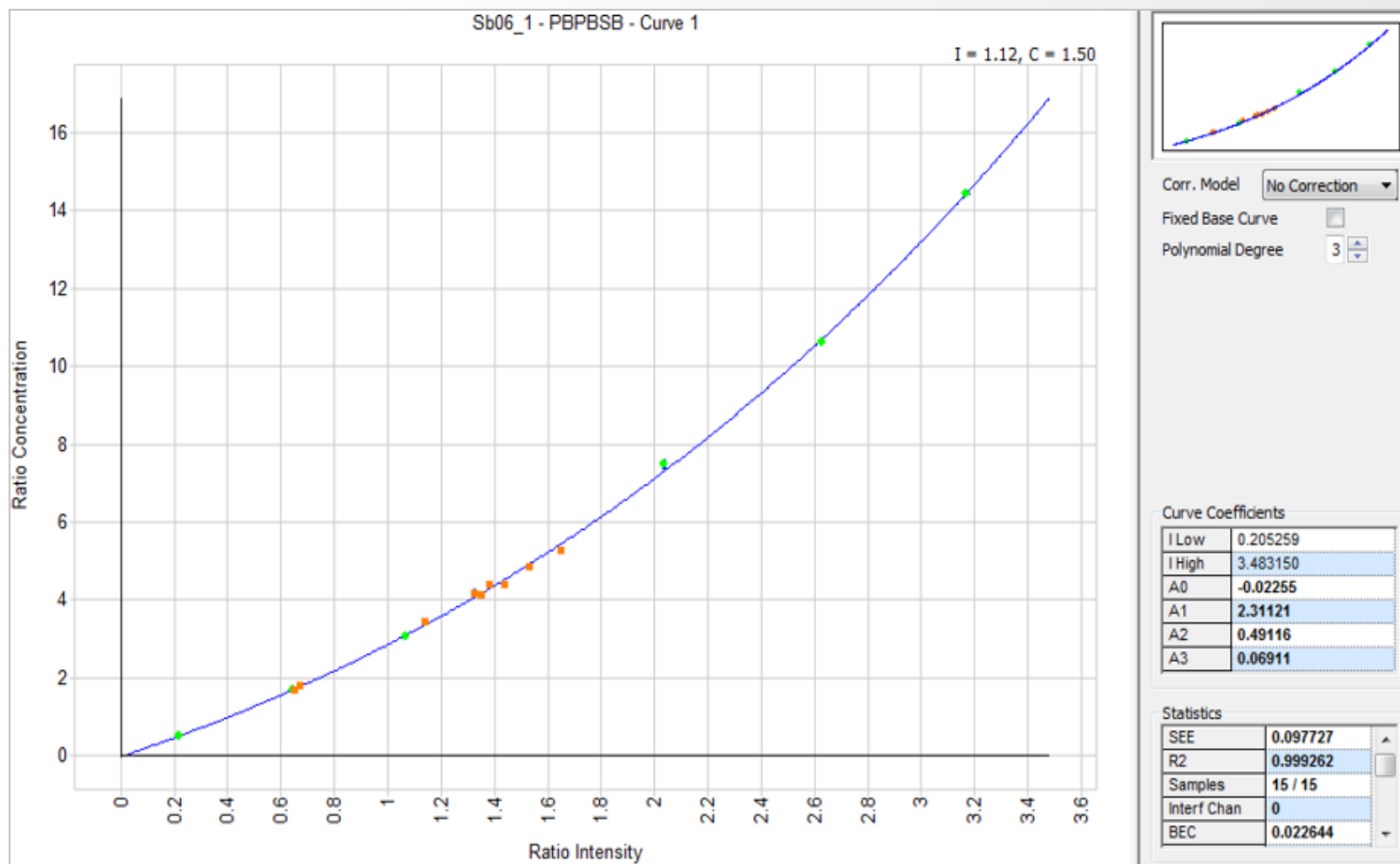# Analysis of lead and its alloys – Calibration example

PbSn

- Sn 2% - 65%
  - 21 samples
  - SEE = 0.4253, C_{max} = 65
  - SEE / C_{max} = 0.0065 (≤ 0.01)
  - R^2 = 0.9997

- Notes
  - SEE is a criterion for accuracy
    - Average difference of the certified concentrations and their values predicted on the curve
    - Accuracy deemed excellent when SEE / C_{max} ≤ 0.01
  - R^2 tells about quality of the fit
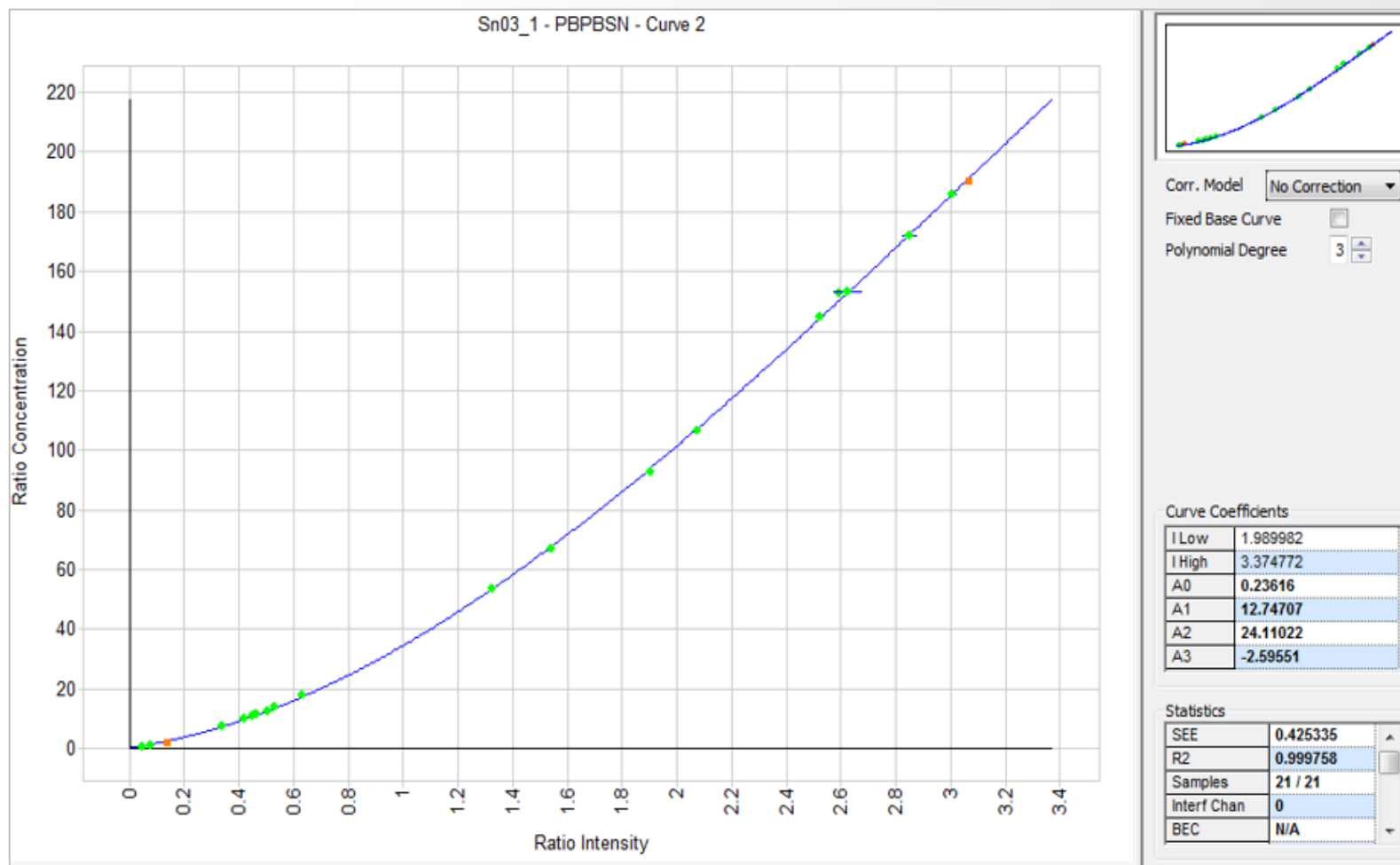
Analysis of lead and its alloys – Calibration example

PbSb

- Sb 0.5% - 12.6%
  - 15 samples
  - SEE = 0.0977, C_{max} = 12.6
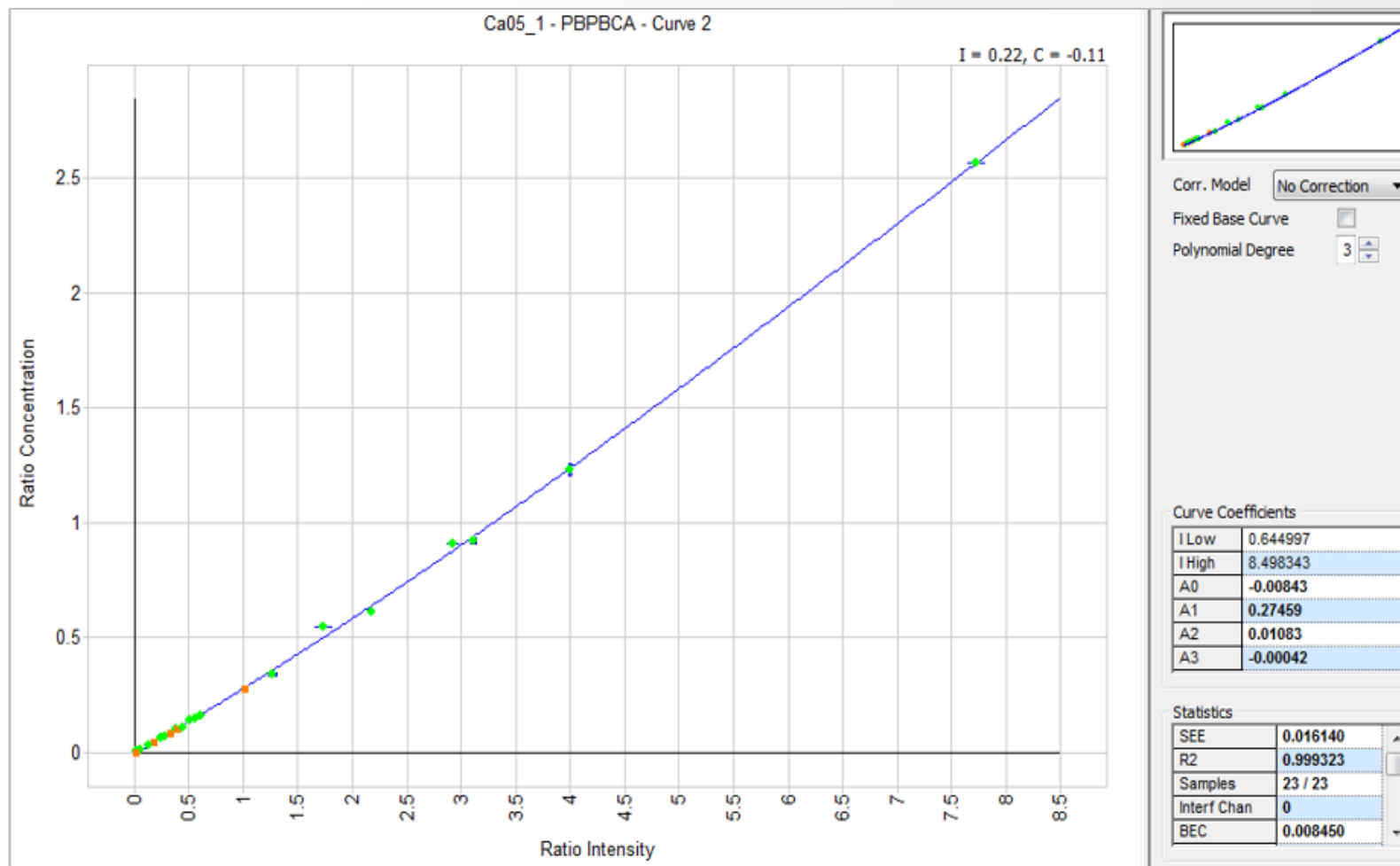 - SEE / C_{max} = 0.0077 (≤ 0.01)
  - R^2 = 0.9993

Analysis of lead and its alloys – Calibration example

PbCa
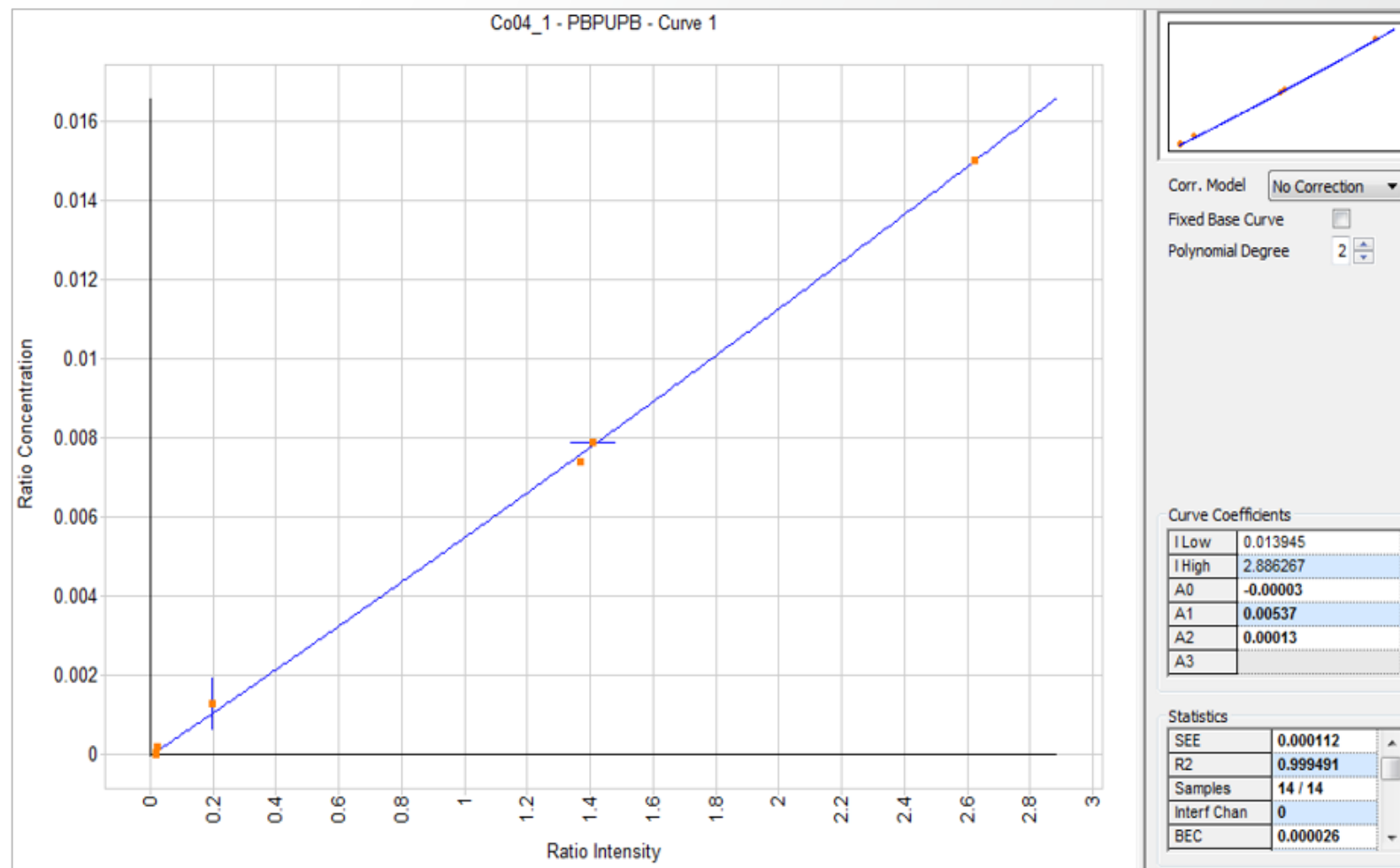
- Ca 0.003% - 2.5%
  - 23 samples
  - SEE = 0.0161, C_{max} = 2.5
  - SEE / C_{max} = 0.0064 (≤ 0.01)
  - R^2 = 0.9993

Analysis of lead and its alloys – Calibration example

Pure Pb

- Co 0.0002% - 0.015%
  - 14 samples (only RMs)
  - SEE = 0.0001, C_{max} = 0.015
  - SEE / C_{max} = 0.0075 (≤ 0.01)
  - R^2 = 0.9995

Analysis of lead and its alloys – Accuracy

Pure lead

- 3 CRMs measured (6-8 runs average)

MBH 83X PR5 C	Pb	Sn	Sb	Bi	Cu	Cd	As	Zn	Ni	Ag	In	Se	Te	Tl
Concentration		0.00028	0.00023	0.0041	0.00038	(0.0001)	0.0003	0.0005	0.00046	0.0008	0.00013	0.00018	0.00023	
Uncertainty (U)		0.0001	0.00006	0.0003	0.00007		0.0001	0.0001	0.00012	0.0002	0.00004	0.00004	0.00006	
Average	99.992	0.00024	0.00025	0.00419	0.00037	0.00000	0.00053	0.00037	0.00002	0.00083	0.00025	0.00023	0.00012	0.00001
Δ/U		0.40	0.33	0.30	0.14		2.30	1.30	3.67	0.15	3.00	1.25	1.83	

BCR 288	Pb	Sn	Sb	Bi	Cu	Cd	As	Zn	Ni	Ag	In	Se	Te	Tl
Concentration		0.00306	0.00325	0.02158	0.00193	0.00333	0.00557	0.00082	0.000457	0.00305		<0.00002	0.00328	0.00023
Uncertainty (U)		0.00015	0.00009	0.00024	0.00004	0.00009	0.00016	0.00004	0.000011	0.00005			0.00013	0.00001
Average	99.952	0.00337	0.00342	0.02144	0.00201	0.00333	0.00601	0.00080	0.00045	0.00303	0.00008	0.00002	0.00339	0.00022
Δ/U		2.07	1.89	0.58	2.00	0.00	2.75	0.50	0.64	0.40			0.85	1.00

BCR 286	Pb	Sn	Sb	Bi	Cu	Cd	As	Zn	Ni	Ag	In	Se	Te	Tl
Concentration			0.00001	0.00215	0.000149	0.0000125		<0.00001	0.0000041	0.0000015				0.00025
Uncertainty (U)			0.000002	0.00005	0.000004	0.0000012			0.0000006	0.0000006				0.00001
Average	99.996	0.00007	0.00003	0.00221	0.000140	0.00001	0.00019	0.00003	0.00002	0.000000	0.00008	0.00005	0.00005	0.00027
Δ/U			10.00	1.20	2.25	2.08			26.50	2.50				2.00

Pb by difference (including 13 additional elements)

- Δ = ABS (Average – Concentration certified) and U = uncertainty on certified concentration

- Accuracy is
  - Excellent   if   Δ/U ≤ 1
  - Very good   if   1 < Δ/U ≤ 2
  - Good   if   2 < Δ/U ≤ 3

Analysis of lead and its alloys – Accuracy

PbSb

- 2 CRMs measured (7-9 runs average)

NIST C241	Pb	Sn	Sb	Bi	Cu	Cd	As	Ni	Ag	Fe	Se	Te	Tl	S
Concentration		0.33	2.95	0.054	0.095	0.002	0.2	<0.001	0.002	<0.001	<0.001	0.0045		0.0026
Uncertainty (U)		0.01	0.04	0.004	0.005	0.001	0.01		0.001			0.0005		0.0007
Average	96.326	0.338	2.977	0.0549	0.0948	0.00168	0.197	0.00064	0.00262	0.00007	0.00000	0.00486	0.00004	0.00247
D/U		0.80	0.68	0.23	0.04	0.32	0.35		0.62			0.72		0.19

BAM EB103	Pb	Sn	Sb	Bi	Cu	Cd	As	Ni	Ag	Fe	Se	Te	Tl	S
Concentration		0.183	1.64	0.0158	0.00097	0.00002	0.097	0.000302	0.0066		0.018	(0.00019)	0.00152	(0.00054)
Uncertainty (U)		0.026	0.06	0.0004	0.00009	0.000008	0.004	0.000027	0.0006		0.001	(0.00006)	0.00007	(0.00012)
Average	97.936	0.181	1.740	0.0161	0.00087	0.000000	0.09872	0.00033	0.00708	0.00009	0.0172	0.00018	0.00152	0.00051
D/U		0.08	1.66	0.62	1.11	2.50	0.43	1.04	0.80		0.77	(6.17)	0.00	(8.75)

- Δ = ABS (Average – Concentration certified) and U = uncertainty on certified concentration

- Accuracy is
  - Excellent   if $\Delta/U \leq 1$
  - Very good   if $1 < \Delta/U \leq 2$
  - Good   if $2 < \Delta/U \leq 3$

Analysis of lead and its alloys – Accuracy

PbCa

- 2 CRMs measured (10 runs average)

BAM 102	Pb	Sn	Sb	Bi	Cu	Cd	As	Zn	Ni	Ag	Ca	In	Se	Al	Te	Au	Na
Concentration		0.895		0.0148	0.00109					0.00248	0.0705			0.0124			
Uncertainty (U)		0.011		0.0005	0.00007					0.00007	0.0011			0.0004			
Average	99.001	0.896	0.00134	0.0150	0.00103	0.00002	0.00022	0.00019	0.00004	0.00253	0.0681	0.00006	0.00016	0.01217	0.00009	0.00007	0.00068
Δ/U		0.08		0.40	0.86					0.71	2.18			0.57			

BAM 101	Pb	Sn	Sb	Bi	Cu	Cd	As	Zn	Ni	Ag	Ca	In	Se	Al	Te	Au	Na
Concentration		0.293		0.0167	0.00173					0.00288	0.1436			0.0257			
Uncertainty (U)		0.007		0.0007	0.00018					0.00007	0.0016			0.0006			
Average	99.509	0.295	0.00025	0.0166	0.00133	0.00002	0.00017	0.00028	0.00004	0.00291	0.1454	0.00009	0.00026	0.0255	0.00011	0.00003	0.00028
Δ/U		0.25		0.16	2.22					0.43	1.10			0.33			

- Δ = ABS (Average – Concentration certified) and U = uncertainty on certified concentration

- Accuracy is
  - Excellent   if Δ/U $\leq$ 1
  - Very good   if   1 < Δ/U $\leq$ 2
  - Good   if   2 < Δ/U $\leq$ 3

For more information

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